

# Reviewing Some Crucial Concepts of Gibbs Energy in Chemical Equilibrium Using a Computer-Assisted, Guided-Problem-Solving Approach

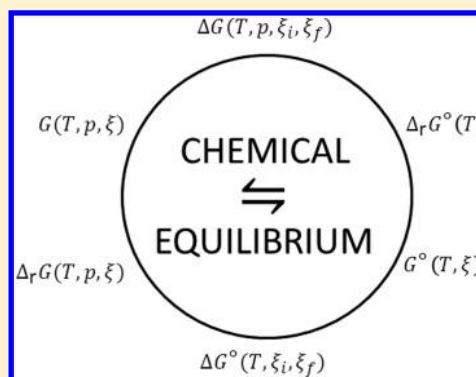
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## S Supporting Information

**ABSTRACT:**  $G$ ,  $G^\circ$ ,  $\Delta_r G$ ,  $\Delta_r G^\circ$ ,  $\Delta G$ , and  $\Delta G^\circ$  are essential quantities to master the chemical equilibrium. Although the number of publications devoted to explaining these items is extremely high, it seems that they do not produce the desired effect because some articles and textbooks are still being written with some of these quantities that appear to be identical to others. This work attempts to clarify the differences between the six quantities using a guided-problem-solving approach instead of a more conventional expository style. A very simple chemical equilibrium,  $\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g})$ , has been chosen as an example. Furthermore, it has been treated in the simplest possible way (as an ideal gas mixture, to thereby avoid fugacities), because the important issue is to sort out concepts and not get entangled in laborious calculations that many times obscure the didactic objective pursued. It is complemented with a small computational tool (a MATLAB script) to quickly perform calculations and graphs. In addition, the script allows one to analyze interactively (through a user-friendly interface) the disturbances that occur in chemical equilibrium owing to changes in temperature and pressure. An exhaustive review of the literature has also been made to select the most useful sources to study this problem.

**KEYWORDS:** Upper-Division Undergraduate, Physical Chemistry, Thermodynamics, Equilibrium, Gases, Problem Solving/Decision Making, Computer-Based Learning



## INTRODUCTION

The central concept in chemistry is the chemical reaction. Chemical reactions are carried out for a very simple reason: to get new compounds, either because they are useful themselves or because they are needed for other reactions. Accordingly, the most important property of a chemical reaction is the feasibility, which is the answer to the following question: what amount of product can be obtained by mixing some initial amounts of reactants and running the process in a specific way? It is often said that a chemical reaction is very feasible if it generates a large amount of product. Thermodynamics, or rather the second law of thermodynamics, provides the answer, and thus, its knowledge is vital for chemists. Gibbsian formulation of classical thermodynamics is the most suitable for chemists. However, many confusions often occur to distinguish between  $G$ ,  $G^\circ$ ,  $\Delta_r G$ ,  $\Delta_r G^\circ$ ,  $\Delta G$ , and  $\Delta G^\circ$ . Mostly this journal, and some others, has made many efforts to correct these errors that are spread in the literature. Most articles are theoretical developments that seek to clarify misconceptions,<sup>1–15</sup> but very few make specific calculations, and those who perform them focus on some specific areas but do not address the problem as a whole<sup>16–23</sup> (a full study of a chemical equilibrium problem is a great opportunity to check if the students have achieved a constructive learning of chemical thermodynamics). This paper does not attempt to expose once again the usual mistakes in the theoretical

concepts but fully solve a concrete example:  $\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g})$ . This paper aims to study the chemical equilibrium using a guided-problem-solving approach. Furthermore, a computational tool (a MATLAB script) has been developed to perform fast calculations and graphics. The pedagogical novelty of this paper is the *manner* that has been arranged to calculate the feasibility of a chemical reaction. *Manner* means: (i) the split of the global procedure into several well-defined stages and (ii) the order in which these stages have been proposed. It is also important to highlight the existence of different mathematical strategies, but nonetheless equivalent, for some stages. The most common errors and incorrect interpretations will be discussed in each stage. This *manner* can be used as a backbone to solve more complex chemical equilibrium problems. The instructor must decide the depth with which he or she wants to use in each task. In the article, an intermediate situation has been chosen. Five or six hours, on average, are sufficient to carry out all tasks (it is understood that the theoretical concepts related to chemical equilibrium have been explained in previous lectures). Students do not have the MATLAB script (its use as a black box should be avoided) while they do these tasks; the script is freely distributed when they finish their work.

## PROBLEM STATEMENT

A single homogeneous chemical reaction in the gas phase is considered:  $\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g})$ . The initial ( $\xi = 0$  mol) amounts of  $\text{N}_2\text{O}_4(\text{g})$  and  $\text{NO}_2(\text{g})$  are 1 and 0 mol, respectively. The process takes place “at constant temperature and pressure”. This phrase is often misunderstood. Enlightening explanations can be found in works by Lewis and Randall,<sup>24</sup> Fain,<sup>25</sup> Denbigh,<sup>26</sup> Anderson,<sup>27</sup> Honig and Ben-Amotz,<sup>28</sup> and Gislason and Craig.<sup>29</sup> It is assumed that  $T = 298.15$  K, and  $p = 10^5$  Pa = 1 bar. The target is to calculate the feasibility of the reaction, defined as the equilibrium value,  $\xi_{\text{eq}}$ , of the extent of reaction,  $\xi$ .

### Task 1: The Domain of the Extent of Reaction

First of all, by simple stoichiometric considerations (see Table 1), it is necessary to calculate the minimum and maximum values of the extent of reaction.<sup>30</sup>

**Table 1. Stoichiometric Analysis of the Problem<sup>a</sup>**

	$\text{N}_2\text{O}_4(\text{g})$	$\rightleftharpoons$	$2\text{NO}_2(\text{g})$
$\xi = 0$ mol	1 mol		0 mol
$\xi = \xi$ mol	$(1 - \xi)$ mol		$2\xi$ mol

<sup>a</sup>Whenever an expression such as  $(1 - \xi)$  appears, it is understood that “1” stands for “1 mol”.

The amount of substance cannot be a negative number. This implies that  $(1 - \xi) \geq 0$  mol, and  $2\xi \geq 0$  mol. In consequence,  $\xi \leq 1$  mol, and  $\xi \geq 0$  mol, that is,  $0 \text{ mol} \leq \xi \leq 1 \text{ mol}$ . These limits are specific for this chemical reaction and these initial amounts of reactants and products. Other numerical examples can be found in the work by Peckham,<sup>31</sup> Levine,<sup>32</sup> and Vandezande et al.<sup>33</sup>

### Task 2: The Thermodynamic Model

Now it is necessary to make a critical decision that completely determines the solution ( $\xi_{\text{eq}}$ ) of the problem. The real chemical system (a gas mixture) must be approximately represented by means of a thermodynamic model. The choice should be made using additional physical information on the system behavior. It is assumed, in this case, as the perfect-gas-mixture (pgm) model defined by the following equation:

$$pV = \left( \sum_B n_B \right) RT \quad (1)$$

$n_B$  is the amount of B ( $n_B = N_B/L$ , where  $N_B$  is the number, dimensionless, of entities of B, and  $L = 6.02214179 \times 10^{23} \text{ mol}^{-1}$  is the Avogadro constant;  $[n_B] = \text{mol}$ ). Experiments show that, at low pressures, this model represents appropriately the behavior of any gas mixture. This choice sets automatically the mathematical expression that allows calculation of the value of the chemical potential of each component in the mixture,  $\mu_B(T, p, x_B) = (\partial G / \partial n_B)_{T, p, n_{j \neq B}}$ . Its SI units are  $\text{J mol}^{-1}$ :

$$\mu_B(T, p, x_B) = \mu_B^\circ(T) + RT \ln \frac{p}{p^\circ} + RT \ln x_B \quad (2)$$

$x_B$  is the mole fraction of B ( $x_B = n_B / \sum_i n_i$ ;  $x_B$  is a dimensionless quantity). Note that  $x_B = f(\xi)$ , that is,  $\mu_B$  is a function of temperature, pressure, and composition.  $p^\circ = 10^5 \text{ Pa} = 1 \text{ bar}$  is the standard pressure and  $\mu_B^\circ(T)$  is the standard ( $p^\circ = 1 \text{ bar}$ ) chemical potential of component B at temperature  $T$ . Note that  $\mu_B^\circ(T)$  is independent of composition. The standard chemical potential is defined in terms of a specified state of aggregation: for a gaseous substance, it is the pure substance in a hypothetical state in which it exhibits ideal gas behavior. The existence of

standard states is a consequence of the impossibility of measuring absolute values of most of the thermodynamic quantities (only changes can be measured). The standard state is the reference used to express these changes.

### Task 3: The Standard Chemical Potential

The next formula is obtained using the definition of the Gibbs energy ( $G = H - TS$ ).

$$\mu_B^\circ(T) = H_{m,B}^\circ(T) - TS_{m,B}^\circ(T) = \Delta_f H_B^\circ(T) - TS_{m,B}^\circ(T) \quad (3)$$

$H_{m,B}^\circ(T) = \mu_B^\circ(T) - T d\mu_B^\circ(T)/dT$  is the standard molar enthalpy of component B at temperature  $T$ , and  $S_{m,B}^\circ(T) = -d\mu_B^\circ(T)/dT$  is the standard molar entropy of component B at temperature  $T$ .  $H_{m,B}^\circ(T)$  may be replaced by  $\Delta_f H_B^\circ(T)$ : the standard enthalpy of formation of component B at temperature  $T$ . Primary thermodynamic tables contain the desired values of  $\Delta_f H_B^\circ(T)$  and  $S_{m,B}^\circ(T)$ . Jacobson<sup>34</sup> has compiled the most widely used. JANAF thermochemical tables<sup>35,36</sup> will be used in this paper to calculate the standard chemical potentials, at 298.15 K, of  $\text{N}_2\text{O}_4(\text{g})$  and  $\text{NO}_2(\text{g})$ .

$$\mu_{\text{N}_2\text{O}_4(\text{g})}^\circ(298.15 \text{ K}) = -81670.7 \text{ J mol}^{-1} \quad (4)$$

$$\mu_{\text{NO}_2(\text{g})}^\circ(298.15 \text{ K}) = -38471.1 \text{ J mol}^{-1} \quad (5)$$

### Task 4: The Feasibility Using a Minimization Procedure

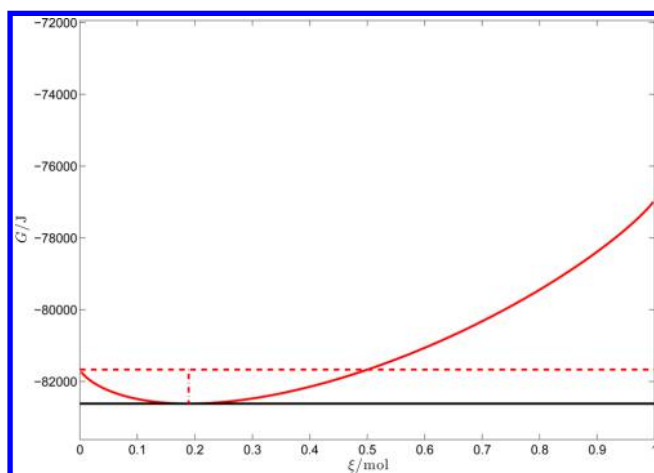
By using the definition of the chemical potential of each component in the mixture (see task 2) and taking into account that the Gibbs energy is an extensive quantity, it is possible to obtain (see details in Levine<sup>37</sup>)

$$G(T, p, \xi) = \sum_B n_B(\xi) \mu_B(T, p, \xi) \quad (6)$$

Note that  $n_B$  is a function of  $\xi$ . By using the information obtained in task 2, this general expression can be particularized to

$$G(T, p, \xi) = (1 - \xi) \left( \mu_{\text{N}_2\text{O}_4(\text{g})}^\circ(T) + RT \ln \frac{1 - \xi}{1 + \xi} + RT \ln \frac{p}{p^\circ} \right) + 2\xi \left( \mu_{\text{NO}_2(\text{g})}^\circ(T) + RT \ln \frac{2\xi}{1 + \xi} + RT \ln \frac{p}{p^\circ} \right) \quad (7)$$

Note that if  $T$  is fixed, the standard chemical potentials of  $\text{N}_2\text{O}_4(\text{g})$  and  $\text{NO}_2(\text{g})$  are known (task 3). If the pressure is also fixed, the Gibbs energy is a function of the extent of reaction only, that is,  $G = G(\xi)$ . “The criterion of equilibrium of a system which is held at constant temperature and pressure is that  $G$  has reached its minimum value”.<sup>26</sup> It is assumed that the system is closed and that there is no work involved other than that related to volume change ( $pV$  work). A simple plot of  $G$  versus  $\xi$  ( $\xi_{\text{min}} = 0$  mol, and  $\xi_{\text{max}} = 1$  mol; see task 1) discovers the equilibrium position ( $\xi_{\text{eq}}$ ): the objective of this problem. The red curve in Figure 1 represents  $G(\xi)$  when  $T = 298.15$  K, and  $p = 1$  bar. At first glance it can be said that  $\xi_{\text{eq}} \approx 0.20$  mol. This low value means that the reaction is not very feasible. It is possible to transform the previous qualitative prediction into a quantitative result: just apply the basic rules of differential calculus:



**Figure 1.**  $n_{\text{N}_2\text{O}_4(\text{g})}(\xi = 0 \text{ mol}) = 1 \text{ mol}$ ,  $n_{\text{NO}_2(\text{g})}(\xi = 0 \text{ mol}) = 0 \text{ mol}$ ,  $T = 298.15 \text{ K}$ , and  $p = 1 \text{ bar}$ . Red curve is  $G$  versus  $\xi$ . Black straight line is the tangent line to the  $G$  versus  $\xi$  curve at  $\xi_{\text{eq}}$ .

$$\left[ \left( \frac{\partial G}{\partial \xi} \right)_{T,p} \right]_{\xi_{\text{eq}}} = 2\mu_{\text{NO}_2(\text{g})}^\circ(T) - \mu_{\text{N}_2\text{O}_4(\text{g})}^\circ(T) + RT \ln \frac{p}{p^\circ} + RT \ln \frac{(2\xi_{\text{eq}})^2}{(1 - \xi_{\text{eq}})(1 + \xi_{\text{eq}})} = 0 \quad (8)$$

It is necessary to calculate the second partial derivative of  $G$  versus  $\xi$ , at  $\xi_{\text{eq}}$ , to ensure that  $G$  is a true minimum at  $\xi_{\text{eq}}$ . This calculation is omitted in the light of the graphical representation shown in Figure 1 (there is no doubt that it is a minimum). By solving eq 8,  $\xi_{\text{eq}} = 0.18918 \text{ mol}$ .

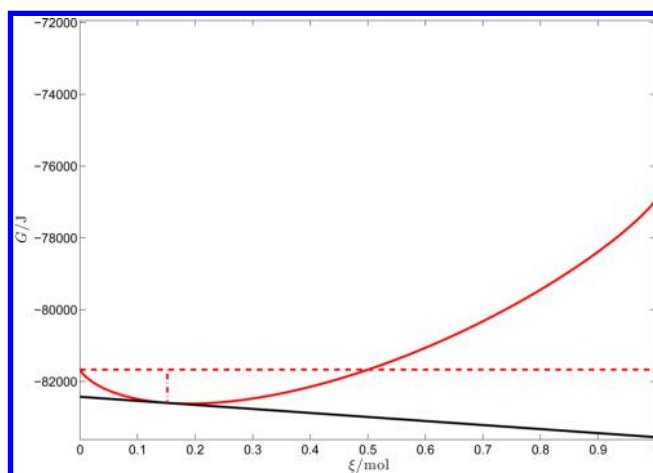
The function  $-(\partial G / \partial \xi)_{T,p}$  is called the affinity<sup>38,39</sup> of the reaction. The affinity is a function of  $T$ ,  $p$ , and  $\xi$ . The reaction stops, as just noted, when the affinity is canceled. The affinity is usually represented as  $-\Delta_r G(\xi)$ , so the condition of equilibrium may be represented as  $\Delta_r G(\xi) = 0$ . The symbol  $\Delta_r$  can be interpreted as the operator  $(\partial / \partial \xi)_{T,p}$ . The black straight line in Figure 1 is the tangent line to the  $G$  versus  $\xi$  curve at  $\xi = \xi_{\text{eq}}$ . The slope of such straight line is the affinity. A careful discussion must be established at this moment. At  $\xi = 0 \text{ mol}$ ,  $G(298.15 \text{ K}, 1 \text{ bar}, 0 \text{ mol}) = -81670.7 \text{ J}$  (a dashed horizontal red straight line represents this value in Figure 1). When the reaction proceeds from  $\xi = 0 \text{ mol}$  to  $\xi_{\text{eq}} = 0.18918 \text{ mol}$ ,  $G(298.15 \text{ K}, 1 \text{ bar})$  reduces its value by  $-949.351 \text{ J}$  (a dashed vertical red straight line represents this value in Figure 1). Then it should be noted that  $\Delta G(298.15 \text{ K}, 1 \text{ bar}, 0 \text{ mol} \rightarrow 0.18918 \text{ mol}) = -949.351 \text{ J}$  (the symbol  $\Delta$  can be interpreted as an increment;  $\Delta X = X_2 - X_1$ ) and not zero as it is often claimed. In Figure 2, the tangent line to the  $G$  versus  $\xi$  curve has been plotted at  $\xi = 0.15179 \text{ mol}$ , an arbitrary value different from  $\xi_{\text{eq}}$ : the black straight line is no longer horizontal (affinity is not zero), and  $\Delta G(298.15 \text{ K}, 1 \text{ bar}, 0 \text{ mol} \rightarrow 0.15179 \text{ mol}) = -929.06 \text{ J}$ .

#### Task 5: The Feasibility Using an Algebraic Procedure

Eq 9 is the Gibbs–Duhem equation at constant  $T$  and  $p$  (see Levine<sup>40</sup>):

$$\sum_B n_B(\xi) d\mu_B(T, p, \xi) = 0 \quad (\text{constant } T \text{ and } p) \quad (9)$$

By using eq 6 as the starting point, taking into account the definition of the extent of reaction ( $n_B = n_B(\xi = 0 \text{ mol}) + \nu_B \xi$ ),



**Figure 2.**  $n_{\text{N}_2\text{O}_4(\text{g})}(\xi = 0 \text{ mol}) = 1 \text{ mol}$ ,  $n_{\text{NO}_2(\text{g})}(\xi = 0 \text{ mol}) = 0 \text{ mol}$ ,  $T = 298.15 \text{ K}$ , and  $p = 1 \text{ bar}$ . Red curve is  $G$  versus  $\xi$ . Black straight line is the tangent line to the  $G$  versus  $\xi$  curve at  $\xi = 0.15179 \text{ mol}$ .

and applying the Gibbs–Duhem equation at constant  $T$  and  $p$  (eq 9), eq 10 is obtained:

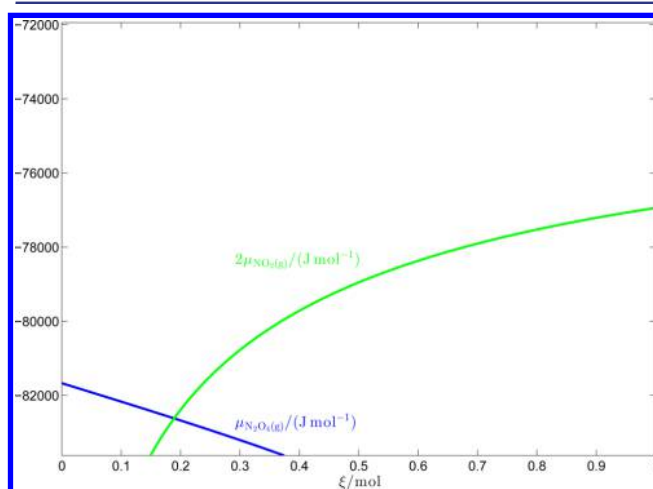
$$\left( \frac{\partial G}{\partial \xi} \right)_{T,p} = \sum_B \nu_B \mu_B(T, p, \xi) \quad (10)$$

$\nu_B$  is the stoichiometric number, dimensionless, of B. It is independent of  $\xi$ . For the reaction considered here,  $\nu_{\text{NO}_2(\text{g})} = 2$ , and  $\nu_{\text{N}_2\text{O}_4(\text{g})} = -1$ . Therefore, the condition of chemical equilibrium is formulated as

$$\sum_B \nu_B \mu_B(T, p, \xi) = 0 \quad (11)$$

Application of this criterion to the specific case developed here results in  $\mu_{\text{N}_2\text{O}_4(\text{g})}(T, p, \xi) = 2 \mu_{\text{NO}_2(\text{g})}(T, p, \xi)$ . A graphical representation can be found in Figure 3.

The green curve is  $2 \mu_{\text{NO}_2(\text{g})}(298.15 \text{ K}, 1 \text{ bar}, \xi)$ , and the blue curve is  $\mu_{\text{N}_2\text{O}_4(\text{g})}(298.15 \text{ K}, 1 \text{ bar}, \xi)$ . Both curves intersect at  $\xi_{\text{eq}} =$



**Figure 3.**  $n_{\text{N}_2\text{O}_4(\text{g})}(\xi = 0 \text{ mol}) = 1 \text{ mol}$ ,  $n_{\text{NO}_2(\text{g})}(\xi = 0 \text{ mol}) = 0 \text{ mol}$ ,  $T = 298.15 \text{ K}$ , and  $p = 1 \text{ bar}$ . Green curve is  $2 \mu_{\text{NO}_2(\text{g})}$  versus  $\xi$ . Blue curve is  $\mu_{\text{N}_2\text{O}_4(\text{g})}$  versus  $\xi$ .

0.18918 mol. Using previous results, the problem can be analytically solved:

$$\frac{\left(\frac{2\xi_{\text{eq}}}{1+\xi_{\text{eq}}}\right)^2 \left(\frac{p}{p^\circ}\right)^2}{\left(\frac{1-\xi_{\text{eq}}}{1+\xi_{\text{eq}}}\right) \left(\frac{p}{p^\circ}\right)} = \exp\left(-\frac{2\mu_{\text{NO}_2(\text{g})}^\circ(T) - \mu_{\text{N}_2\text{O}_4(\text{g})}^\circ(T)}{RT}\right)$$

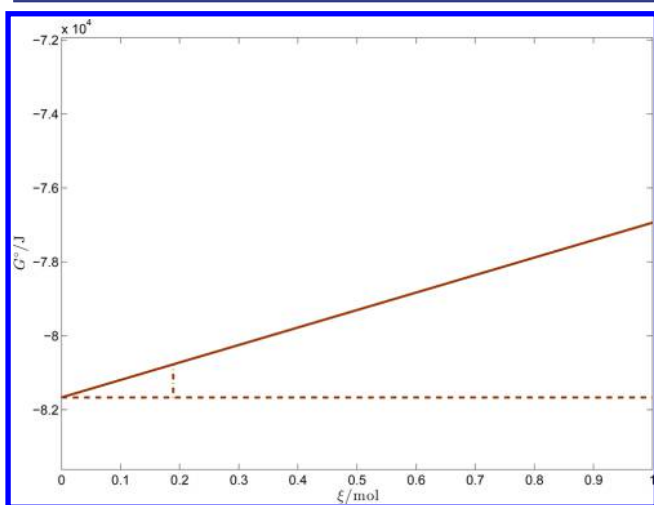
$$= \exp\left(-\frac{\Delta_r G^\circ(T)}{RT}\right) \quad (12)$$

It is interesting to point out that a new quantity,  $\Delta_r G^\circ(T) = 2\mu_{\text{NO}_2(\text{g})}^\circ(T) - \mu_{\text{N}_2\text{O}_4(\text{g})}^\circ(T)$ , has appeared. Its name is the standard reaction Gibbs energy, and it is a function only of temperature.<sup>41</sup> At 298.15 K, its value is 4728.43 J mol<sup>-1</sup> (a fairly widespread misconception is to consider the units of the standard reaction Gibbs energy as J). Once this value is known, it is very easy (if compared to task 4) to obtain  $\xi_{\text{eq}} = 0.18918$  mol. It is worthy to note that  $\Delta_r G^\circ(298.15 \text{ K}) > 0$ ; however, the reaction proceeds until  $\xi_{\text{eq}} = 0.18918$  mol. One of the most common mistakes is to qualify as “not spontaneous” those reactions with  $\Delta_r G^\circ(T) > 0$ . It is true that the reaction is not very feasible, but  $\xi_{\text{eq}} \neq 0$  mol. B. F. Dodge<sup>42</sup> has established a set of qualitative rules that classify the chemical reactions according to their feasibility. It is very important to realize that feasibility is a global property: it is assigned to the reaction (for given conditions of pressure and temperature, the reaction is slightly or highly feasible). However, spontaneity is a local property represented by  $\Delta_r G(\xi)$ ; for given conditions of pressure and temperature, it depends on the extent of reaction. If  $\Delta_r G(\xi) < 0$ ,  $\xi$  will increase (“spontaneous to the right”) up to  $\xi_{\text{eq}}$ . If  $\Delta_r G(\xi) > 0$ ,  $\xi$  will decrease (“spontaneous to the left”) to  $\xi_{\text{eq}}$ . Equation 13 follows immediately from eq 6:

$$G^\circ(T, \xi) = \sum_B n_B(\xi) \mu_B^\circ(T) \quad (13)$$

The brown straight line in Figure 4 represents  $G^\circ(298.15 \text{ K}, \xi)$ .

At  $\xi = 0$  mol,  $G^\circ(298.15 \text{ K}, 1 \text{ bar}, 0 \text{ mol}) = -81670.7 \text{ J}$  (a dashed horizontal brown straight line represents this value in Figure 4). This value is identical to  $G(298.15 \text{ K}, 1 \text{ bar}, 0 \text{ mol})$ . When the reaction proceeds from  $\xi = 0$  mol to  $\xi_{\text{eq}} = 0.18918$  mol,  $G^\circ(298.15 \text{ K}, \xi)$  increases its value by 894.50 J (a dashed vertical brown straight line represents this value in Figure 4). Then it



**Figure 4.**  $n_{\text{N}_2\text{O}_4(\text{g})}(\xi = 0 \text{ mol}) = 1 \text{ mol}$ ,  $n_{\text{NO}_2(\text{g})}(\xi = 0 \text{ mol}) = 0 \text{ mol}$ ,  $T = 298.15 \text{ K}$ , and  $p = 1 \text{ bar}$ . Brown straight line is  $G^\circ$  versus  $\xi$ .

should be noted that  $\Delta_r G^\circ(298.15 \text{ K}, 0 \text{ mol} \rightarrow 0.18918 \text{ mol}) = 894.50 \text{ J}$ .

Note that in the study of chemical equilibrium, there are six different quantities that contain the letter  $G$ :  $G(T, p, \xi)$ ,  $G^\circ(T, \xi)$ ,  $\Delta_r G(T, p, \xi)$ ,  $\Delta_r G^\circ(T)$ ,  $\Delta G(T, p, \xi_i, \xi_j)$ , and  $\Delta G^\circ(T, \xi_i, \xi_j)$ .

#### Task 6: The Standard Equilibrium Constant: A New Way To Obtain Feasibility Using an Algebraic Procedure

The procedure developed in task 5 can be presented in a simpler manner by introducing the standard equilibrium constant,  $K^\circ(T)$ :

$$\Delta_r G^\circ(T) = -RT \ln K^\circ(T) \quad (14)$$

At 298.15 K, its value is

$$K^\circ(298.15 \text{ K}) = \exp\left(-\frac{\Delta_r G^\circ(298.15 \text{ K})}{RT}\right) = 0.14846 \quad (15)$$

Note that the standard equilibrium constant is a dimensionless quantity and is a function of temperature only. For a perfect-gas-mixture,

$$K^\circ(\text{pgm}, T) = \prod_B \left(\frac{x_B^{\text{eq}} p}{p^\circ}\right)^{\nu_B} \quad (16)$$

If  $p = 1 \text{ bar}$ , eq 16 can be simplified to

$$K^\circ(\text{pgm}, T) = \prod_B (x_B^{\text{eq}})^{\nu_B} \quad (17)$$

By combining eqs 15 and 17, it is possible to obtain the value of  $\xi_{\text{eq}}$ :

$$K^\circ(\text{pgm}, T) = \frac{\left(\frac{2\xi_{\text{eq}}}{1+\xi_{\text{eq}}}\right)^2}{\left(\frac{1-\xi_{\text{eq}}}{1+\xi_{\text{eq}}}\right)} \rightarrow \xi_{\text{eq}}$$

$$= (1 \text{ mol}) \sqrt{\frac{K^\circ(\text{pgm}, 298.15 \text{ K})}{4 + K^\circ(\text{pgm}, 298.15 \text{ K})}}$$

$$= 0.18918 \text{ mol} \quad (18)$$

The work done so far is summarized below. The goal of tasks 4, 5, and 6 is to get the value of  $\xi_{\text{eq}}$  (the feasibility of the chemical reaction). Task 4 is, substantially, a straightforward application of the second law of thermodynamics to systems “at constant temperature and pressure”. Task 5 is a special formulation of task 4 when the thermodynamic system is a chemical reaction. Task 6 is a user-friendly presentation (and it is therefore the method chosen by chemists to calculate the feasibility of a chemical reaction) of task 5. Table 2 summarizes the essential thermodynamic quantities (along with their symbols, definitions, SI units, and brief comments) discussed so far.

#### Task 7: Alternative Procedure To Calculate the Standard Reaction Gibbs Energy

The standard reaction Gibbs energy, the decisive quantity in these calculations, has been defined in eq 12. However, it is very common to find other formulas to get  $\Delta_r G^\circ(T)$ :

$$\Delta_r G^\circ(T) = \sum_B \nu_B \Delta_f G_B^\circ(T) \quad (19)$$

It should be emphasized that  $\mu_B^\circ(T) \neq \Delta_f G_B^\circ(T)$ . The standard Gibbs energies of formation of  $\text{NO}_2(\text{g})$  and  $\text{N}_2\text{O}_4(\text{g})$  are

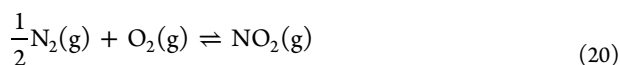


Table 2. Summary of Essential Quantities<sup>a</sup> To Master Chemical Equilibrium

Quantity	Symbol	Definition	SI Units	Comments
Gibbs energy	$G$	$\sum_B n_B \mu_B$	J	The relationship between the chemical potential and the standard chemical potential depends on the thermodynamical model.
Standard Gibbs energy	$G^\circ$	$\sum_B n_B \mu_B^\circ$	J	There are different definitions for the standard chemical potential of a gas, a liquid, a solid and the solute and the solvent in a solution.
Gibbs energy change	$\Delta G$	$G_{\xi_f} - G_{\xi_i}$	J	The symbol $\Delta$ can be interpreted as a finite difference: $\Delta X = X_f - X_i$ .
Standard Gibbs energy change	$\Delta G^\circ$	$G_{\xi_f}^\circ - G_{\xi_i}^\circ$	J	The symbol $\Delta$ can be interpreted as a finite difference: $\Delta X = X_f - X_i$ .
Affinity of reaction	$-\Delta_r G$	$-\left(\frac{\partial G}{\partial \xi}\right)_{T,p} = -\sum_B \nu_B \mu_B$	J mol <sup>-1</sup>	The symbol $\Delta_r$ can be interpreted as the operator $(\partial/\partial \xi)_{T,p}$ .
Standard reaction Gibbs energy	$\Delta_r G^\circ$	$\left(\frac{\partial G^\circ}{\partial \xi}\right)_{T,p} = \sum_B \nu_B \mu_B^\circ$	J mol <sup>-1</sup>	The symbol $\Delta_r$ can be interpreted as the operator $(\partial/\partial \xi)_{T,p}$ .

<sup>a</sup>Mathematical definitions for the Gibbs energy and the standard Gibbs energy are particular expressions for the case we considered (a homogeneous reaction mixture). Similarly, mathematical definitions for the Gibbs energy change and the standard Gibbs energy change are particular expressions for a chemical reaction.

calculated (data have been extracted from JANAF thermochemical tables<sup>35</sup>) below:



$$\begin{aligned} \Delta_f G_{\text{NO}_2(\text{g})}^\circ(T) &= \mu_{\text{NO}_2(\text{g})}^\circ(T) - \frac{1}{2} \mu_{\text{N}_2(\text{g})}^\circ(T) - \mu_{\text{O}_2(\text{g})}^\circ(T) \\ &= H_{\text{NO}_2(\text{g})}^\circ(T) - TS_{\text{NO}_2(\text{g})}^\circ(T) \\ &\quad - \left[ \frac{1}{2} (H_{\text{N}_2(\text{g})}^\circ(T) - TS_{\text{N}_2(\text{g})}^\circ(T)) + (H_{\text{O}_2(\text{g})}^\circ(T) - TS_{\text{O}_2(\text{g})}^\circ(T)) \right] \end{aligned} \quad (21)$$

$$\begin{aligned} \Delta_f G_{\text{NO}_2(\text{g})}^\circ(298.15 \text{ K}) &= 33095 - 298.15 \times 240.03 \\ &\quad - \left[ \frac{1}{2} (0 - 298.15 \times 191.609) \right. \\ &\quad \left. + (0 - 298.15 \times 205.147) \right] \end{aligned} \quad (22)$$

$$\begin{aligned} \Delta_f G_{\text{NO}_2(\text{g})}^\circ(298.15 \text{ K}) &= 51257.7 \text{ J mol}^{-1} \\ &\neq \mu_{\text{NO}_2(\text{g})}^\circ(298.15 \text{ K}) = -38471.1 \text{ J mol}^{-1} \end{aligned} \quad (23)$$

$$\begin{aligned} \text{N}_2(\text{g}) + 2\text{O}_2(\text{g}) &\rightleftharpoons \text{N}_2\text{O}_4(\text{g}) \quad (24) \\ \Delta_f G_{\text{N}_2\text{O}_4(\text{g})}^\circ(T) &= \mu_{\text{N}_2\text{O}_4(\text{g})}^\circ(T) - \mu_{\text{N}_2(\text{g})}^\circ(T) - 2\mu_{\text{O}_2(\text{g})}^\circ(T) \\ &= H_{\text{N}_2\text{O}_4(\text{g})}^\circ(T) - TS_{\text{N}_2\text{O}_4(\text{g})}^\circ(T) \\ &\quad - [(H_{\text{N}_2(\text{g})}^\circ(T) - TS_{\text{N}_2(\text{g})}^\circ(T)) + 2(H_{\text{O}_2(\text{g})}^\circ(T) - TS_{\text{O}_2(\text{g})}^\circ(T))] \end{aligned} \quad (25)$$

$$\begin{aligned} \Delta_f G_{\text{N}_2\text{O}_4(\text{g})}^\circ(298.15 \text{ K}) &= 9079 - 298.15 \times 304.376 \\ &\quad - [(0 - 298.15 \times 191.609) \\ &\quad + 2(0 - 298.15 \times 205.147)] \end{aligned} \quad (26)$$

$$\begin{aligned} \Delta_f G_{\text{N}_2\text{O}_4(\text{g})}^\circ(298.15 \text{ K}) &= 97786.7 \text{ J mol}^{-1} \\ &\neq \mu_{\text{N}_2\text{O}_4(\text{g})}^\circ = -81670.7 \text{ J mol}^{-1} \end{aligned} \quad (27)$$

However, the standard Gibbs energies of formation may be used to calculate the standard reaction Gibbs energy because the difference between them (appropriately weighted with the stoichiometric numbers) cancels the terms in square brackets in eqs 22 and 26. Standard Gibbs energies of formation are directly tabulated in primary thermodynamic tables so they are the preferred option for calculating the standard reaction Gibbs energy.

#### Task 8: Partial Molar Quantities

As mentioned in task 4, the black straight line (Figure 1) is the tangent line to the  $G$  versus  $\xi$  curve at  $\xi = \xi_{\text{eq}}$ . It is simple to deduce the general (arbitrary  $\xi$ ) equation of this straight line. Suppose that  $G = G_\alpha$  at  $\xi = \xi_\alpha$ . Eq 28 is the equation of the line that is tangent to  $G$  at  $\xi_\alpha$ :

$$\frac{G - G_\alpha}{\xi - \xi_\alpha} = -\mu_{\text{N}_2\text{O}_4(\text{g})}(\xi_\alpha) + 2\mu_{\text{NO}_2(\text{g})}(\xi_\alpha) \quad (28)$$

Using eq 6,

$$G_\alpha = (1 - \xi_\alpha)\mu_{\text{N}_2\text{O}_4(\text{g})}(\xi_\alpha) + 2\xi_\alpha\mu_{\text{NO}_2(\text{g})}(\xi_\alpha) \quad (29)$$

Combining eqs 28 and 29,

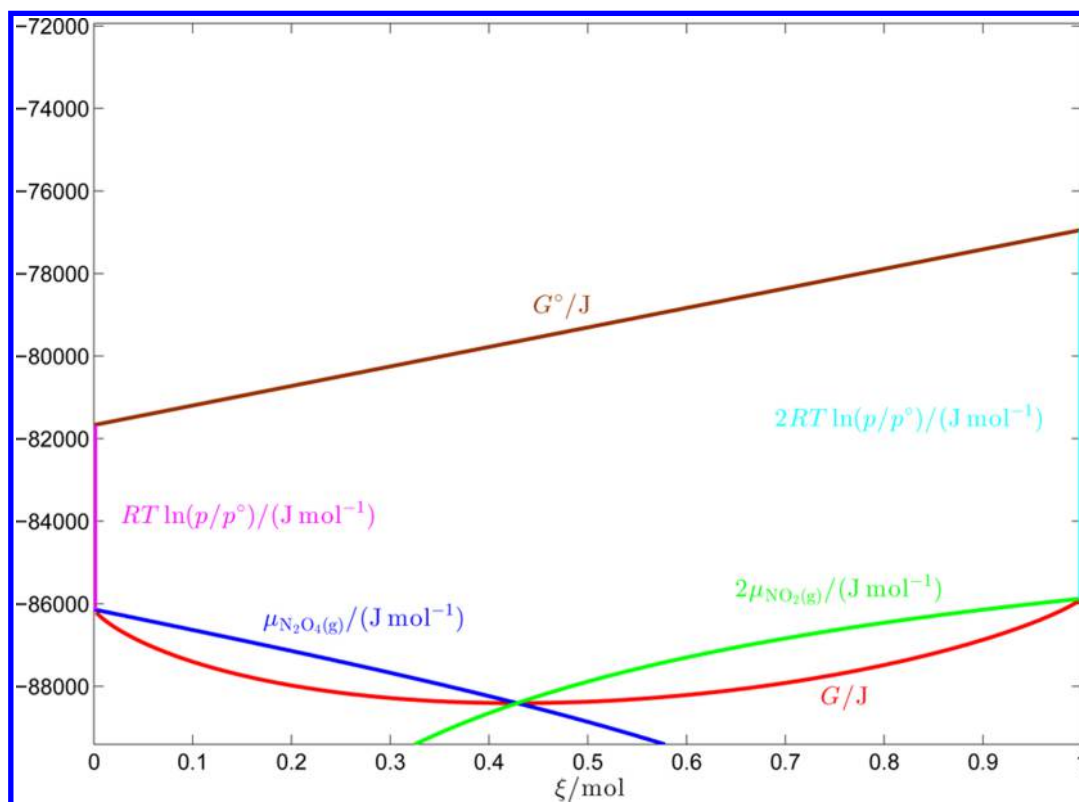
$$\begin{aligned} G &= (1 - \xi_\alpha)\mu_{\text{N}_2\text{O}_4(\text{g})}(\xi_\alpha) + 2\xi_\alpha\mu_{\text{NO}_2(\text{g})}(\xi_\alpha) \\ &\quad + [-\mu_{\text{N}_2\text{O}_4(\text{g})}(\xi_\alpha) + 2\mu_{\text{NO}_2(\text{g})}(\xi_\alpha)](\xi - \xi_\alpha) \\ &= (1 - \xi)\mu_{\text{N}_2\text{O}_4(\text{g})}(\xi_\alpha) + \xi 2\mu_{\text{NO}_2(\text{g})}(\xi_\alpha) \end{aligned} \quad (30)$$

It is worthy to note that

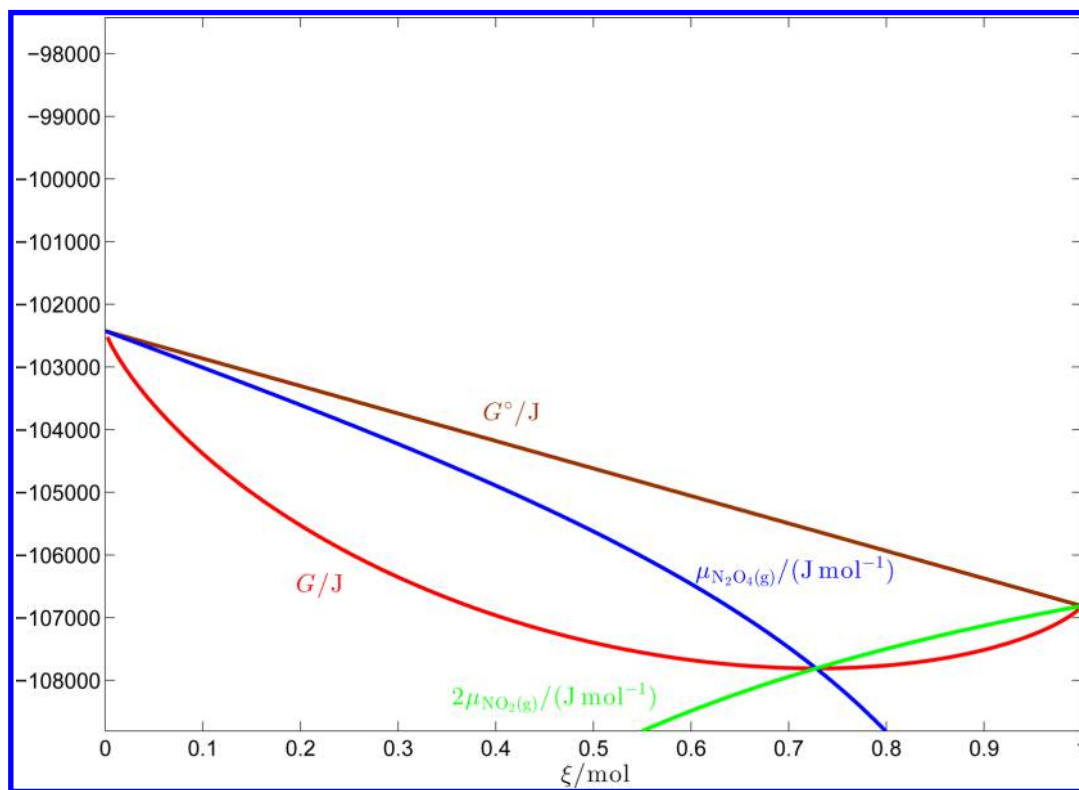
$$\xi = 0 \text{ mol} \rightarrow G = 1 \text{ mol} \times \mu_{\text{N}_2\text{O}_4(\text{g})}(\xi_\alpha) \quad (31)$$

$$\xi = 1 \text{ mol} \rightarrow G = 1 \text{ mol} \times 2 \times \mu_{\text{NO}_2(\text{g})}(\xi_\alpha) \quad (32)$$

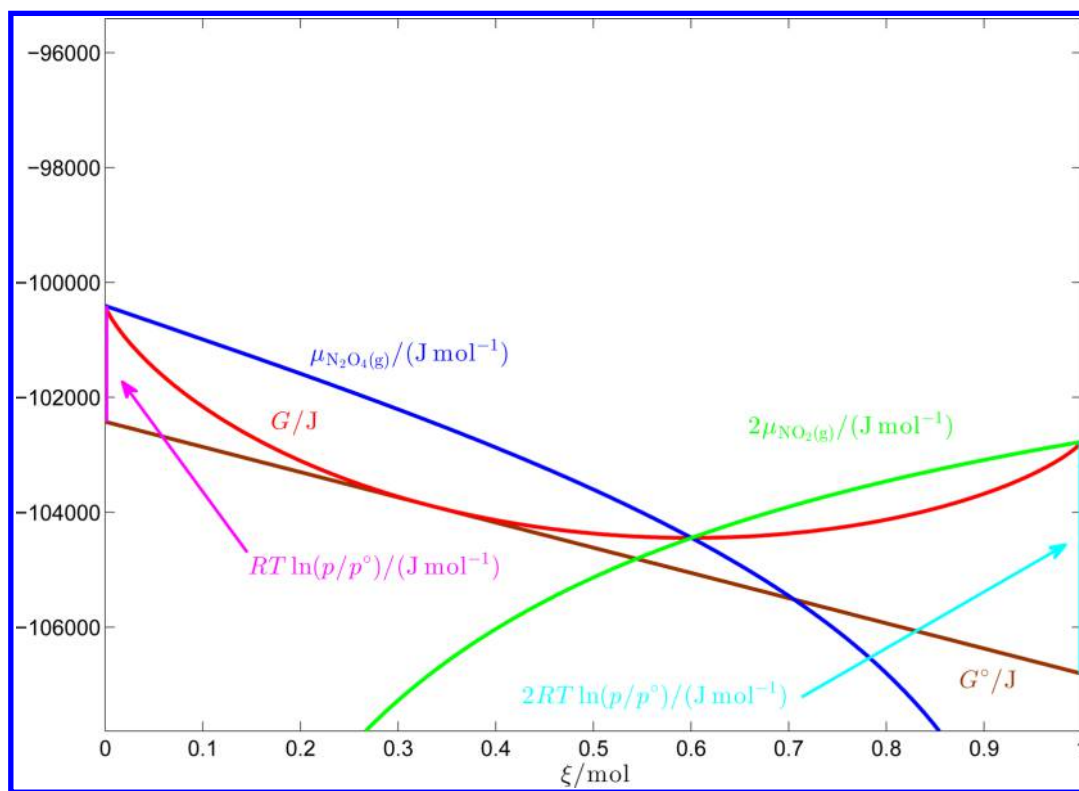
Eqs 31 and 32 are obtained by considering  $\xi = 0 \text{ mol}$  or  $\xi = 1 \text{ mol}$  in eq 30. This means that the intersections of the tangent line (black color) with the vertical lines drawn at  $\xi = 0 \text{ mol}$  and  $\xi = 1 \text{ mol}$  correspond with  $\mu_{\text{N}_2\text{O}_4(\text{g})}(\xi_\alpha)$  and  $2\mu_{\text{NO}_2(\text{g})}(\xi_\alpha)$ . In Figure 1, the tangent line is calculated at  $\xi = \xi_{\text{eq}}$ ; hence,



**Figure 5.**  $n_{\text{N}_2\text{O}_4(\text{g})}(\xi = 0 \text{ mol}) = 1 \text{ mol}$ ,  $n_{\text{NO}_2(\text{g})}(\xi = 0 \text{ mol}) = 0 \text{ mol}$ ,  $T = 298.15 \text{ K}$ , and  $p = 0.165 \text{ bar}$ . Red, green, and blue curves represent  $G$ ,  $2\mu_{\text{NO}_2(\text{g})}$ , and  $\mu_{\text{N}_2\text{O}_4(\text{g})}$ , respectively (always versus  $\xi$ ). Brown straight line represents  $G^\circ$  versus  $\xi$ . The gap between the brown straight line and the rest of the curves (pointed out by magenta and cyan straight lines) is due to the difference between  $p$  and  $p^\circ$ .



**Figure 6.**  $n_{\text{N}_2\text{O}_4(\text{g})}(\xi = 0 \text{ mol}) = 1 \text{ mol}$ ,  $n_{\text{NO}_2(\text{g})}(\xi = 0 \text{ mol}) = 0 \text{ mol}$ ,  $T = 350.15 \text{ K}$ , and  $p = 1 \text{ bar}$ . Red, green, and blue curves represent  $G$ ,  $2\mu_{\text{NO}_2(\text{g})}$ , and  $\mu_{\text{N}_2\text{O}_4(\text{g})}$ , respectively (always versus  $\xi$ ). Brown straight line represents  $G^\circ$  versus  $\xi$ .



**Figure 7.**  $n_{\text{N}_2\text{O}_4(\text{g})}(\xi = 0 \text{ mol}) = 1 \text{ mol}$ ,  $n_{\text{NO}_2(\text{g})}(\xi = 0 \text{ mol}) = 0 \text{ mol}$ ,  $T = 350.15 \text{ K}$ , and  $p = 2 \text{ bar}$ . Red, green, and blue curves represent  $G$ ,  $2\mu_{\text{NO}_2(\text{g})}$ , and  $\mu_{\text{N}_2\text{O}_4(\text{g})}$ , respectively (always versus  $\xi$ ). Brown straight line represents  $G^\circ$  versus  $\xi$ . Note, again, the gap between the brown straight line and the rest of the curves (pointed out by magenta and cyan straight lines).

$$\begin{aligned} 2\mu_{\text{NO}_2(\text{g})}(298.15 \text{ K}, 1 \text{ bar}, \xi_{\text{eq}}) \\ = \mu_{\text{N}_2\text{O}_4(\text{g})}(298.15 \text{ K}, 1 \text{ bar}, \xi_{\text{eq}}) = -82620.1 \text{ J mol}^{-1} \end{aligned} \quad (33)$$

In Figure 2, the tangent line is calculated at  $\xi = 0.15179 \text{ mol} \neq \xi_{\text{eq}}$  (the tangent line is not horizontal):

$$\begin{aligned} -83553.2 \text{ J mol}^{-1} &= 2\mu_{\text{NO}_2(\text{g})}(298.15 \text{ K}, 1 \text{ bar}, 0.15179 \text{ mol}) \\ &\neq \mu_{\text{N}_2\text{O}_4(\text{g})}(298.15 \text{ K}, 1 \text{ bar}, 0.15179 \text{ mol}) \\ &= -82429.1 \text{ J mol}^{-1} \end{aligned} \quad (34)$$

### Task 9: Pressure Changes

The feasibility of the reaction changes if the pressure is altered. If the actual pressure is  $p$  (instead of  $p^\circ$ ), the mathematical procedure described in task 6 changes to

$$\begin{aligned} K^\circ(\text{pgm}, T) &= \frac{\left(\frac{2\xi_{\text{eq}}}{1+\xi_{\text{eq}}}\right)^2 \left(\frac{p}{p^\circ}\right)^2}{\left(\frac{1-\xi_{\text{eq}}}{1+\xi_{\text{eq}}}\right) \left(\frac{p}{p^\circ}\right)} \rightarrow \xi_{\text{eq}} \\ &= (1 \text{ mol}) \sqrt{\frac{(K^\circ(\text{pgm}, T)p^\circ/p)}{4 + (K^\circ(\text{pgm}, T)p^\circ/p)}} \end{aligned} \quad (35)$$

Let  $T = 298.15 \text{ K}$  and  $p = 0.165 \text{ bar}$ . By applying eq 35,  $\xi_{\text{eq}} = 0.42853 \text{ mol}$  (see Figure 5).

The feasibility has undergone a substantial change. Note that  $T$  has not changed, so the standard equilibrium constant,  $K^\circ$  (pgm, 298.15 K), remains fixed. The same applies to the standard

reaction Gibbs energy,  $\Delta_r G^\circ$  (298.15 K). Using  $\Delta_r G^\circ$  (298.15 K)  $> 0$ , when  $p \neq p^\circ$ , to describe the reaction as “nonspontaneous” is a double error. It is not correct to associate  $\Delta_r G^\circ$  with spontaneity (as mentioned in task 5). It is also incorrect to use standard quantities when  $p \neq p^\circ$ . Additionally, the pressure change has generated a significant change in the graphical representation shown in Figure 5.  $G^\circ$  (298.15 K,  $\xi$ ) has not suffered, obviously, any disturbance (it is a function of the temperature only), but the rest of the elements have been moved. The source of this change is in the term  $RT \ln(p/p^\circ)$ , which now is not null (see eq 2). The vertical magenta and cyan lines represent the contribution of this term.

### Task 10: Temperature Changes

Temperature changes also alter the feasibility of the reaction. Now, the fundamental quantities (standard equilibrium constant and standard reaction Gibbs energy) change. The calculations must be redone from the beginning. Figure 6 shows the traditional analysis that is being done in this paper when  $T = 350.15 \text{ K}$ , and  $p = p^\circ = 1 \text{ bar}$ . The feasibility has changed to  $0.72807 \text{ mol}$  (JANAF thermochemical tables<sup>35</sup> provides thermodynamic data at this temperature), which is a relatively high value. Van’t Hoff equation is another alternative for these calculations.<sup>43–45</sup> Its use has been prevalent in the past, but with computers available, its use does not make sense (pedagogical reasons excluded).

### Task 11: Temperature and Pressure Changes

Drastic effects are observed if temperature and pressure change. Figure 7 shows the results when  $T = 350.15 \text{ K}$ , and  $p = 2 \text{ bar}$ . The feasibility has changed to  $0.60052 \text{ mol}$ .

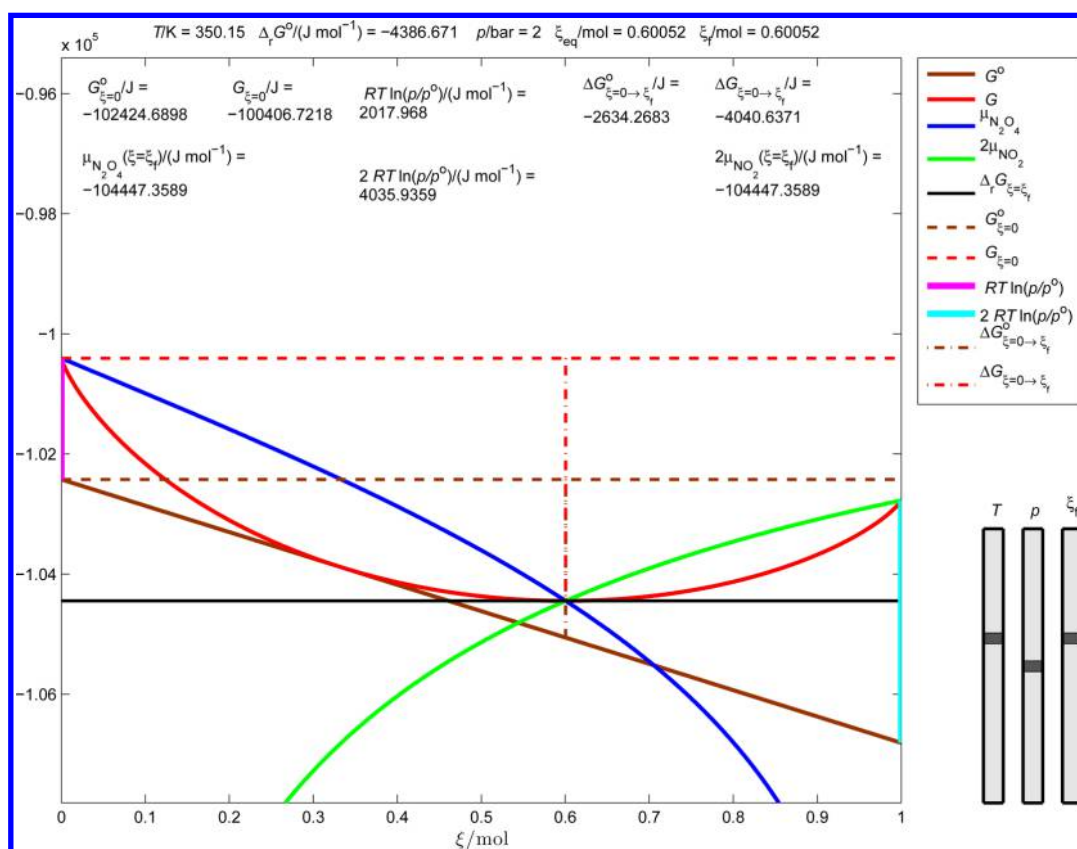


Figure 8.  $n_{\text{N}_2\text{O}_4(\text{g})}(\xi = 0 \text{ mol}) = 1 \text{ mol}$ ,  $n_{\text{NO}_2(\text{g})}(\xi = 0 \text{ mol}) = 0 \text{ mol}$ ,  $T = 350.15 \text{ K}$ , and  $p = 2 \text{ bar}$ . Output of the *vce.m* script.

### Task 12: A Final Digression, Entropy Analysis

Clearly, the problem can be solved using the second law of thermodynamics in its most general form. In this case, the system and the surroundings must be studied (see details in Bindel<sup>46</sup>).

#### THE MATLAB SCRIPT VCE.M

The visual chemical equilibrium script (*vce.m*) is a MATLAB code that has been developed to simultaneously perform all the calculations and graphics described in this paper (except those described in task 12). The script needs two input files: thermodynamic data of  $\text{N}_2\text{O}_4(\text{g})$  and  $\text{NO}_2(\text{g})$ . A cubic spline interpolation procedure has been established to obtain thermodynamic data not included in the input files; different alternatives<sup>47,48</sup> are also possible (although they have not been implemented). To begin, the user must enter the temperature and the pressure. The output of the script is shown in Figure 8.

The first and second vertical sidebars allow the user to alter (dragging the black stripe) the values of temperature and pressure (the exact numerical values appear at the top of the graph) and see immediately the effects that occur on the feasibility ( $\xi_{\text{eq}}$ ) of the reaction. The script also allows (using the third vertical sidebar) the user to plot the tangent of the  $G$  versus  $\xi$  curve at different values of  $\xi$  (the code initially plots the tangent at  $\xi_{\text{eq}}$ ). The variation ranges of these quantities are predetermined in the script but can be easily changed. The script is included in the Supporting Information.

#### CONCLUSIONS

A very simple chemical equilibrium ( $\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g})$ ) has been fully studied (numerically and graphically) from different perspectives. The applied methodology has been a guided-

problem-solving approach instead of a traditional expository method. The most common errors in the interpretation of the thermodynamic properties have been identified. A MATLAB script (with a user-friendly interface) has been developed to facilitate all tasks. An exhaustive review of the literature has also been performed to select the sources that, according to the author, become clearer to study this problem.

#### ASSOCIATED CONTENT

##### Supporting Information

MATLAB main and auxiliary scripts (*vce.m*, *Movep.m*, *MoveT.m*, *Moveξif.m*, *recalculate.m*, and *rtslid.m*) and thermodynamic data files (*janaf\_nitrogendioxide.txt* and *janaf\_nitrogenetraoxide.txt*). This material is available via the Internet at <http://pubs.acs.org>.

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##### Notes

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